Methods for the Collection and Measurement of Chromophoric Dissolved Organic Matter (CDOM) and Dissolved Organic Carbon (DOC)

Reference for DOC and CDOM methods:
Mannino, A., M. E. Russ, and S. B. Hooker (2008), Algorithm development and validation for satellite-derived distributions of DOC and CDOM in the U.S. Middle Atlantic Bight, J. Geophys. Res., 113, C07051, doi:10.1029/2007JC004493.

Seawater samples for analysis of dissolved organic carbon (DOC) and chromophoric dissolved organic matter (CDOM) absorption are filtered under a gentle vacuum (<5 in Hg) through pre-combusted (6 hours at 450°C) Whatman GF/F glass fiber filters and collected directly into pre-cleaned and pre-combusted sample glass bottles and vials. Triplicate samples at the surface and duplicate samples at depth are collected for DOC analysis and stored frozen. DOC is measured in duplicate or triplicate at the surface approximately 20 percent of the samples at depth are run in duplicate. They are measured by high temperature combustion oxidation using a Shimadzu TOC-V with 3 of 7 injections to maintain a standard deviation <2% (Benner and Strom 1993; Sharp et al. 2002; Mannino et al. 2008). The deep Sargasso Sea water or Florida Straight water certified reference material (Hansell Laboratory, University of Miami RSMAS) is used daily to verify the accuracy of DOC measurements and maintain an analytical error to within ±5%.

The deep seawater CRM measurements for batch 5 2010 and batch 12 2011 analyzed with these samples (44.0 ± 2.3 mmol C L^{-1}; n = 35) were within 5% of reported values (41–44 mmol C L^{-1}). The average % CV for the reps measured was 3.32%. Standard curves of the manufacturer-recommended carbon standard (potassium hydrogen phthalate) ranging from ~500 to 4000 µg C L^{-1} and from ~500 to 2000 µg C L^{-1} are conducted daily. Furthermore, standards are interspersed between every 6 samples for each sample batch to verify the consistency of the standard curve throughout each sample batch analyzed. The instrument carbon blank is determined from the area counts of the numerous Milli-Q ultraviolet oxidized ultra-pure water injections. The instrument carbon blank is subtracted from each sample and deep sea reference standard. To minimize salt accumulation in the TOC-V flow path, Milli-Q water blanks are inserted between every 3 samples for each batch of samples. Injection volumes for seawater samples, standards and blanks are typically 120µL.

Samples for determination of CDOM spectral absorption coefficients are stored under refrigeration. In the laboratory, CDOM samples are warmed to room temperature and filtered through 0.2 µm Whatman Nuclepore polycarbonate filters or Sartorius (polyethersulfone) filters prior to analysis (Mitchell et al. 2000). Filtration of CDOM samples through GF/F filters is necessary for coastal ocean waters due to the high particle load that quickly clog Nuclepore and Supor filters. Absorption spectra of CDOM are measured using a Agilent 4000 UV-Visible scanning spectrophotometer (250-800 nm) with UV oxidized Milli-Q water as the blank and reference (Mitchell et al. 2003). Instrument scan settings were as follows: 250–800 nm wavelength scan range, 1 nm data interval, 100 nm min^{-1} scan rate, and 4 nm slit width. The instrument noise for reference baselines of air-to-air and ultrapure water spectral scans was within ±0.0005 absorbance units. Spectral absorption coefficients are determined after subtracting the raw absorption measurements with field filtration blanks of UV-oxidized Milli-Q and a null point value an average of absorbance for 650-680nm (modified from Mitchell et al.

2000; 2003). Where absorption spectra of filtration blanks are within the level of instrument noise, additional corrections are not necessary. Instrument performance tests (wavelength accuracy and reproducibility, photometric noise, and baseline flatness) were conducted each day prior to analysis. Furthermore, National Institute of Standards and Technology (NIST)-traceable calibration standards (Holmium oxide filter for wavelength accuracy and Spectronics standards, Thermo Electron Corporation, to evaluate stray light, wavelength accuracy, and photometric performance) were also used to verify instrument performance. The uncertainty associated with CDOM spectral absorption coefficients at an instrument noise level $<0.0046\ m^{-1}$ was on the order of 0.023 to 0.039 m^{-1} and based on the summation of the instrument manufacturer's guaranteed specifications for photometric accuracy, stability and noise.

Repeat scans of seawater subsamples, replicate subsamples, and Niskin versus persistaltic pump samples yielded a coefficient of variation of typically $<\pm 3\%$.

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